

Spin Catalysis: Quantitative Kinetics

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Abstract—The rate constants of radical recombination catalyzed by organic radicals are an order of magnitude greater than the rate constants of noncatalytic recombination. The catalytic efficiency of paramagnetic lanthanide ions is much lower than that of organic radicals and is proportional to the electron spin of the ions. This linear correlation is in accordance with the spin catalysis theory.

INTRODUCTION

Retention of the total angular moment of electrons and nuclei in chemical reactions involving spin carriers (radicals, paramagnetic ions, and high-spin molecules) is the fundamental principle of the chemical dynamics resulting in electron and nuclear spin selectivity of the chemical reaction and in a difference between chemical reactivities of spin states of reagents. Three types of interactions can change the spin of reagents and transform spin-forbidden states of the precursor of the reaction into chemically active spin-allowed states [1, 2]:

- (1) magnetic interaction of the electron spin with the nuclear spin and an external magnetic field (hyperfine and Zeeman splitting);
- (2) interaction between the electron spin of the high-spin precursor (for example, a triplet radical pair) and the magnetic component of the microwave field;
- (3) exchange interaction of the pair of electron spins with the electron spin of an alien spin carrier.

The former two interactions are the sources of the previously known magnetic effects [3], and the latter induces a new phenomenon: spin catalysis of radical recombination.

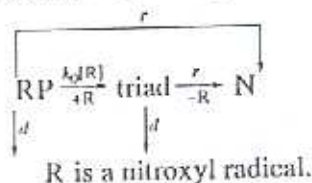
It has been recently shown that one of the partners in the radical triad enhances the reactivity of the pair of other partners. For example, the probability of the recombination of the triplet radical pair $[\text{PhCH}(\text{CH}_3)\dot{\text{C}}\text{O}\dot{\text{C}}\text{H}(\text{CH}_3)\text{Ph}]$ generated by the photolysis of *d,l*-diphenylpentan-3-one (DPP) in benzene increases in the presence of the stable nitroxyl radical TEMPO [4]. A similar effect is observed for the recombination of alkyl radicals with biradicals: the reactivity of the radical centers of the biradical is higher than that of the corresponding monoradical fragments [5]. In all cases, three radicals participate in chemical transformations, and the odd radical acts as the spin catalyst rather than the radical acceptor.

The theoretical analysis of the three-spin model [6] confirms that the exchange interaction between the partners of the radical triad stimulates spin evolution between the doublet spin states of the triad and results in the oscillating triplet-singlet conversion of the radical pair chosen in the triad under the action of the odd radical spin. Acceleration of the triplet-singlet conversion of the radical pair under the action of the third spin is the physical basis for the spin-catalytic effect, which even predominates over the traditional function of the third radical as the acceptor of the radical pair. The spin-catalytic effect in radical recombination was also observed in the presence of paramagnetic ions [7-9].

In this work, we suggest the kinetic analysis of spin-catalytic effects in recombination of radical pairs, the derivation of kinetic equations, and quantitative estimation of the rate constants of catalytic recombination referred to the rate constants of noncatalytic recombination and discuss the value of the effect as a function of the spin of the spin catalyst.

SPIN CATALYSIS BY RADICALS

Figure 1 shows that the probability of recombination of the radical pair of DPP increases in the presence of nitroxyl radicals. This indicates two parallel routes of the spin transformation of the radical pair: the "native" route induced by magnetic interactions inside the pair (hyperfine, Zeeman, dipole, etc.) and the catalytic route stimulated by nitroxyl radicals (Scheme I).



Scheme I.

Scheme I summarizes these two channels of spin transformation in terms of the kinetic rate constants. The direct transformation of the radical pair RP into the

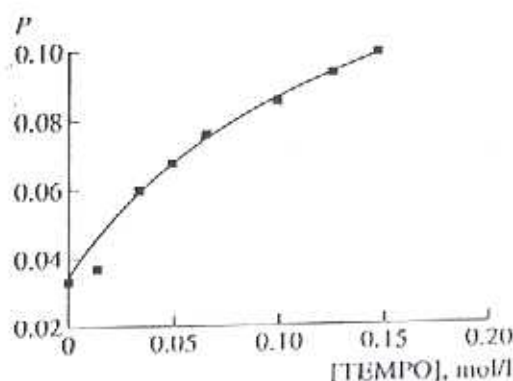


Fig. 1. Dependence of the probability of recombination (P) of the radical pair $[\text{PhCH}(\text{CH}_3)\dot{\text{C}}\text{O}\dot{\text{C}}\text{H}(\text{CH}_3)\text{Ph}]$ generated by the photolysis of DPP in benzene on the concentration of TEMPO [4].

product of recombination N with the rate constant r is accompanied by the catalytic transformation, which includes incorporation of the nitroxyl radical in RP with the diffusion rate constant k_0 followed by the transformation of the radical triad into the product N with the rate constant r^* . The diffusion dissociation of RP and radical triad, which decomposes them, is characterized by the rate constant d .

In terms of Scheme I, the probability of recombination (P_{RP}) via the first, noncatalytic route is determined by the expression:

$$P_{\text{RP}} = r / (r + d + k_0[\text{R}]). \quad (1)$$

The probability of the transformation of RP into the radical triad reads:

$$P_u = k_0[\text{R}] / (r + d + k_0[\text{R}]), \quad (2)$$

and the probability of the transformation of the triad into the reaction product N is equal to

$$P_u^* = r^* / (r^* + d). \quad (3)$$

The total probability of the recombination of RP obeys the equation

$$P = P_{\text{RP}} + P_u + P_u^*. \quad (4)$$

Substituting (1)–(3) into (4), we can easily derive the resulting equation

$$P = \frac{r}{r + d + k_0[\text{R}]} + \frac{r^*}{r^* + d} \frac{k_0[\text{R}]}{d + k_0[\text{R}] + r}. \quad (5)$$

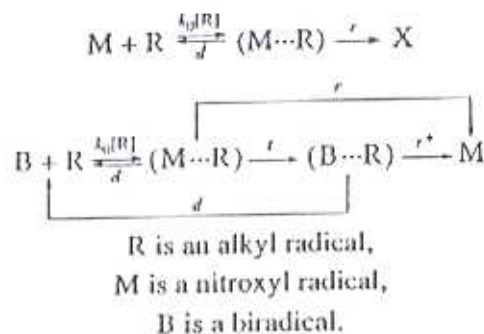
At $[\text{R}] = 0$, the P value is equal to 0.033 (see Fig. 1), so that the ratio $r/d = 0.033$. It is clear that when $r \ll d$, equation (5) transforms into equation (6)

$$P = \frac{r}{d + k_0[\text{R}]} + \frac{r^*}{r^* + d} \frac{k_0[\text{R}]}{d + k_0[\text{R}]}. \quad (6)$$

The quantitative analysis of the experimental data presented in Fig. 1 using equation (6) results in the correlation $r^*/r = 6.3 \pm 0.1$, which is retained when the rate constant k_0 is changed within reasonable limits from 10^{10} to 10^8 l/mol.

The ratio $r^*/r = 6.3$ is a quantitative measure of the spin-catalytic efficiency and demonstrates that the recombination rate constant of RP in the radical triad is almost an order of magnitude higher than that in the isolated RP.

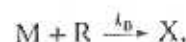
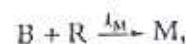
Now let us analyze quantitatively the spin catalysis in the reaction of biradicals with alkyl radicals [5].



Scheme II.

Scheme II describes the sequence of elementary steps of accepting alkyl radicals R by the nitroxyl monoradical M and biradical B. Scheme II implies the collision of M and R to form the pair (M...R), which can recombine to the reaction product X or dissociate with the rate constant d . The reaction between B and R includes the formation of the pair (M...R) due to the collision of R with one of the radical centers of the biradical. This pair can dissociate and recombine (with the rate constants d and r , respectively) or transform into the triad (B...R) if another radical center of the biradical enters the radical pair (M...R) with the rate constant t . It is assumed that the triad recombines to give a monoradical or dissociates with liberation of the alkyl radical or one of the radical centers of the biradical. Note that Scheme II does not consider the direct formation of the triad (B...R) by the collision of R with B. The reason is that the nitroxyl biradicals studied in [5] exist predominantly in extended molecular conformations in which the radical centers of the biradicals are remote, so that the probability of the collision of the alkyl radical with the geminal conformation of N is negligible when both radical centers of the biradical are brought together.

The combination of Scheme II with the phenomenological kinetic scheme of two reactions considered in [5],



allows one to obtain the following expressions for the rate constants k_M and k_B :

$$k_M = \frac{k_0 r}{r+d}; \quad k_B = \frac{k_0 r^* t}{(d+t+r)(d+r)} + \frac{k_0 r}{d+t+r} \quad (7)$$

Taking into account the evident correlations $r \ll d$, $r^* \ll d$, and $t \ll d$, the ratio of the rate constants of catalytic and noncatalytic recombination can be derived from equations (7):

$$r^*/r = (\varphi - 1)(d/t), \quad (8)$$

where $\varphi = k_B/k_M$ and, according to estimates made in [5], ranges from 1.1 to 1.5. Since the extended molecular conformations of biradicals predominate, it is expected that the rate constant t is at least an order of magnitude lower than the rate constant of the escape of the biradical from the triad (B...R). It can be assumed that the latter has the same order of magnitude as the rate constant of dissociation d . These arguments confirm the validity of the correlation $t \ll d$; therefore, it immediately follows from equation (8) that $r^*/r \gg 1$. When the reasonable limits of 50–10 are accepted for the t/d ratio, and $\varphi = 1.1$ –1.5 [5], the r^*/r ratio falls in the 5–25 range, which agrees with the same ratio for the radical pair generated by the photolysis of DPP in benzene (which was discussed above). Lacking information on the numerical values of t and d (or their ratio) rules out a more exact estimate of the r^*/r ratio.

SPIN CATALYSIS BY PARAMAGNETIC IONS

The authors of [8] found the effect of paramagnetic lanthanide ions on the photolysis of *p*-methylidibenzylketone in sodium dodecyl sulfate (SDS) micelles:



where A = PhCH₂, and B = *p*-CH₃PhCH₂. The yield of the cage product AB, i.e., the cage effect (CE), depends on the concentration of lanthanide ions (Fig. 2).

The cage effect is related to the recombination of the secondary radical pair of alkyl radicals A and B formed from the primary pair by decarbonylation: CE is identical to the probability of recombination P of this secondary pair. Figure 2 shows that the addition of lanthanide ions results in an increase in CE (and hence, in P); however, the efficiencies of different ions in the acceleration of the recombination process are different. For Eu³⁺, La³⁺, and Lu³⁺, weak dependences of CE and P on the concentration are caused by a change in the micelle size upon addition of ions rather than by the spin catalysis. Our goal is to estimate quantitatively the efficiency of lanthanide ions. Note that the dependence of CE (or P) on the ion concentration is similar to that shown in Fig. 1 for the probability of recombination of RP in the presence of nitroxyl radicals as spin catalysts. In order to use the results presented in Fig. 2 and to adapt the dependence of P on the ion concentration to equation (6), the concentrations of the ions in a micellar solution should be referred to their concentration in the micelles, taking into account that the binding constants

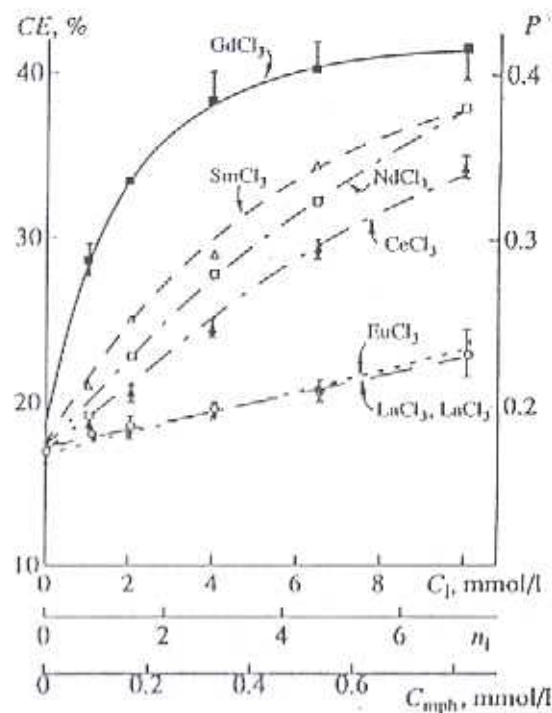


Fig. 2. Dependences of the cage effect CE and the probability of recombination P on the concentration of lanthanide ions [8] in a micellar solution C_1 and in the micellar phase C_{mph} and on the average number of ions added to the individual micelle n_i .

of the ions with micelles are greater than 10^5 l/mol, so that more than 99% of ions are added to the micelles. The average number of the ions in each micelle is determined by the evident correlation:

$$n_i = C_1 / (C_m / n_m), \quad (9)$$

where C_1 is the concentration of ions in a micellar solution; C_m is the concentration of DDS molecules; and n_m is the aggregation number, i.e., the average number of DDS molecules in the micelle. Knowing the micelle radius r_0 and, hence, its volume, we can calculate the concentration of the ions in the micellar phase C_{mph} , which is not equivalent to the concentration in the micellar solution. Of course, this approach to determine the concentrations of additives in micelles is disputable; however, the arguments in favor of this approach will be presented later.

For the particular case of DDS, we have $n_m = 50$ [10], $C_m = 70$ mmol/l [8], $r_0 = 15.4$ Å [11], and the n_i values calculated from (9) and C_{mph} are shown in Fig. 2. It is noteworthy that lanthanide ions as spin catalysts are much weaker than nitroxyl radicals: in order to achieve a noticeable catalytic effect, each micelle should contain several ions ($n_i \gg 1$), so that the concept of the ion concentration in the micellar phase C_{mph} , which was used above, is quite substantiated.

Now equation (6) can be easily transformed into (10):

Ratios r^*/r for lanthanide ions

Ion	Spin S	r^*/r	Ion	Spin S	r^*/r
La ³⁺	0	0	Tb ³⁺	3	0.93
Ce ³⁺	1/2	0.34	Dy ³⁺	5/2	0.78
Pr ³⁺	1	0.28	Ho ³⁺	2	0.62
Nd ³⁺	3/2	0.71	Er ³⁺	3/2	0.47
Pm ³⁺	2	—	Tm ³⁺	1	0.31
Sm ³⁺	5/2	0.93	Yb ³⁺	1/2	0.31
Eu ³⁺	3	0	Lu ³⁺	0	0
Gd ³⁺	7/2	3.4			

$$P = \frac{r}{r + d + k_0 C_{\text{mph}}} + \frac{r^* k_0 C_{\text{mph}}}{r^* + dr + d + k_0 C_{\text{mph}}}, \quad (10)$$

where P designates CE (Fig. 2), and other constants are identical to the constants in equation (6); it should be kept in mind that they are related to the micellar phase, but not to the micellar solution. The following correlations for Gd³⁺ ions can be easily derived from equation (10) and Fig. 2:

$$P(C_{\text{mph}} = 0) = r/(r + d) = 0.17,$$

$$P(C_{\text{mph}} \rightarrow \infty) = r^*/(r^* + d) = 0.41.$$

The combination of these equations gives the ratio $r_{\text{Gd}}^*/r = 3/4$, i.e., even the spin catalyst, which is most efficient among lanthanide ions, is almost half as efficient in the spin transformation of the pair as the organic nitroxyl radical.

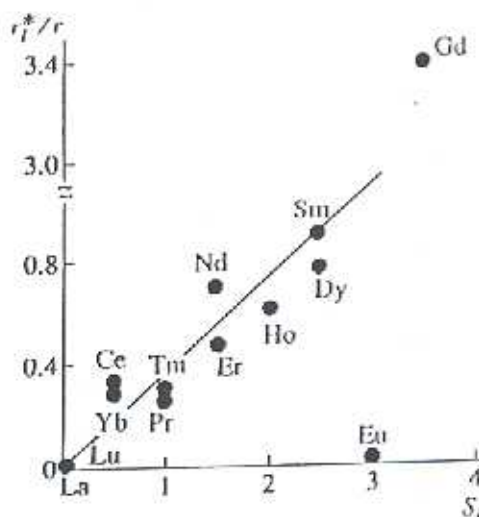


Fig. 3. Ratios of rate constants of catalytic r_i^* and noncatalytic r recombination of the radical pair as a function of spin S_i of lanthanide ions. Experimental data were obtained for the magnetic field of 2000 G.

This direct calculation method is hardly appropriate for other ions, because the curve of the dependence of P on C_{mph} does not reach saturation, unlike the case with Gd³⁺ ions. Therefore, we should use the experimental data presented in Fig. 2, substituting them directly into equation (10) similar to that for nitroxyl radicals (see previous Section).

The numerical analysis of equation (10) shows that the conditions $r^* \ll d$, $r \ll k_0 C_{\text{mph}}$, and $r^* \ll k_0 C_{\text{mph}}$ are fulfilled at low concentrations of ions, $C_{\text{mph}} \leq 0.2$ mol/l for which the slopes in the initial regions of the curves of the $P(C_{\text{mph}})$ dependences, characterizing the relative catalytic efficiency of different ions, were measured in [8]. Then, equation (10) takes the form:

$$P = r/d + (r^* k_0/d^2) C_{\text{mph}}, \quad (11)$$

It follows from this equation that the initial slopes of the $P(C_{\text{mph}})$ curves are proportional to r^* . The r_i^*/r_{Gd}^* ratios and then the r_i^*/r^* ratios can be determined by referring the slopes in the initial regions for ions of the i type to the corresponding value for Gd³⁺.

These ratios for different ions are summarized in the table and are presented in Fig. 3 as a function of the ion spin S_i . This figure demonstrates the correlation between the efficiency of the ion as the spin catalyst and its electron spin. The correlation indicates unambiguously, according to the theory [6], that the exchange interaction between the partners (the radical pair, on the one hand, and the paramagnetic ion, on the other hand) is responsible for the spin-catalyzed recombination of the pair. The absence of a correlation between the efficiency of the ions and their magnetic moment mentioned in [8] provides an additional argument in favor of the concept of spin catalysis.

CONCLUSION

The kinetic analysis of the spin-catalytic effect differentiates spin carriers with respect to their capability of producing spin transformation of radical pairs. Organic radicals, i.e., spin carriers with an external unpaired electron, were found to be most efficient. For these carriers, the ratio $r^*/r = 10$, i.e., the presence of the spin catalyst in the radical pair accelerates its spin conversion by an order of magnitude. Lanthanide ions are much less efficient, and their r_i^*/r ratios fall in the 0.2–1.0 range; i.e., the contribution of the spin-catalytic effect to the spin conversion of the pair does not exceed 20–100% of the contribution of the noncatalytic, magnetically induced channel.

The low efficiency of ions as spin catalysts can result from inaccessibility of internal unpaired electrons partially screened by external electrons. The only exception is Gd³⁺, which was unexpectedly found to be a high-efficiency spin catalyst ($r^*/r = 3.5$) with a similar efficiency to organic radicals. The unique position

of Eu^{3+} , which possesses six unpaired electrons but has no spin-catalytic effect, was discussed in [8] and can be ascribed to the fact that this ion in the ground electronic state is diamagnetic due to the compensation of the spin and orbital magnetic moments.

As a mechanism of spin conversion of a radical pair, the spin catalysis competes with the magnetically induced spin conversion and, hence, leads to the suppression of magnetic-field effects in reactions of pairs. This phenomenon was distinctly demonstrated in [9] for the photolysis of deoxybenzoin and its derivatives in DDS micelles. Moreover, it was established that the efficiency of lanthanide ions in the suppression of magnetic-field effects was parallel to their spin-catalytic efficiency. It should also be mentioned that the Mn^{2+} ion as a spin catalyst is comparable with Gd^{3+} .

The difference between spin-catalytic efficiencies of spin carriers agrees perfectly with the theory predicting that the rate of spin conversion of a pair is proportional to the difference between the exchange energies between the spin catalyst and each of the partners of the radical pair [6]. This suggests that spin carriers with external unpaired electrons are much more preferable as spin catalysts than spin carriers with internal unpaired electrons. However, on the other hand, the former carriers, which are efficient spin catalysts, are also usually chemically reactive radical acceptors, whereas the latter carriers, which are low-efficiency spin catalysts, are chemically inert. The strategy of the spin catalysis is, in fact, a compromise between these two functions of the spin carrier: to be simultaneously a spin catalyst and a spin acceptor.

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